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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE:

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SUBJECT: PPfs 1E2443 and 1E2444 Glyphosate on guavas and papayas, respectively.
Evaluation of the analytical method and residue data.

FROM: K. H. Arne, Ph.D., Chemist *K.H. Arne*
Residue Chemistry Branch (TS-769)

TO: Clinton Fletcher, Product Manager No. 43
Emergency Response Section
Registration Division (TS-767)

and

Toxicology Branch
Hazard Evaluation Division (TS-769)

THRU: Charles L. Trichilo, Chief
Residue Chemistry Branch (TS-769) *A. J. Schmitt*

Interregional Research Project No. 4, Dr. M. E. Burt, Assistant Coordinator and Dr. R. H. Kupelian, National Director, State Agricultural Experiment Station, Rutgers University, New Brunswick, NJ, on behalf of the IR-4 Technical Committee and the Agricultural Experiment Station of Hawaii proposes tolerances for glyphosate (Roundup®, N-phosphonomethylglycine) on guavas and papayas, both at 0.2 ppm.

Tolerances for glyphosate (which includes the parent and aminomethylphosphonic acid, a metabolite) are established for several RACs ranging from 0.1 ppm for the liver and kidneys of cattle, goats, horses, hogs, sheep and poultry to 15 ppm for soybean forage and hay (Section 180.364).

Conclusions

1. The nature of the residue is adequately understood. In both plants and animals the residue of concern consists of the parent and a metabolite, aminomethylphosphonic acid.
2. N-nitrosoglyphosate is an impurity in the formulated product. The presence of N-nitrosoglyphosate (NNG) in the formulated material has been subjected to a hazard assessment review with the result that OPP does not bar the establishment of glyphosate tolerances because of the presence of this impurity.
3. Adequate analytical methods are available for enforcement of the proposed tolerance.
4. From the proposed use to the orchard floor, we expect no detectable residue of parent or aminomethylphosphonic acid metabolite (<0.05 ppm each) in papayas or guavas.
5. Since no feed items are involved, there will be no problem of secondary residues in meat, milk, poultry and eggs.

6. An International Residue Limit Status sheet is attached. No tolerances for guava or papaya are established outside the U.S. The Canadian limit for glyphosate (which includes the parent only) on stone fruits is 0.1 ppm.

7. TOX has recently expressed concern over the level of [] is an impurity in a surfactant inert ingredient in the formulation. Little, if any residue of [] would be expected in the fruits from the proposed use. [] is cleared as an inert ingredient under 40 CFR 180.1001(d) when used as a solvent or cosolvent.

Recommendation

Toxicological considerations permitting, we recommend for the proposed tolerances. TOX has recently withheld their support from this petition (memo of 2/5/81, W. Dykstra) until questions about the levels of dioxane contamination are resolved.

Detailed Considerations

Manufacture & Formulation

The manufacturing process for technical glyphosate has previously been submitted (PP#6E1809) and detailed in our reviews (e.g., D. Duffy, review of 11/30/76, PP#6G1826).

The technical product is formulated as an aqueous concentrate containing 41% of the isopropylamine salt of glyphosate. This formulation, trade name Roundup®, contains 4 lbs of the isopropylamine salt per gallon which is equivalent to 3 lbs glyphosate per gallon.

The inert ingredients in this formulation consist of the surfactant [] (cleared under 40 CFR 180.1001 (d)).

[] which are not expected to present any residue problem.

An additional impurity in the formulated product (an impurity in the technical product as well) is N-nitrosoglyphosate (NNG) which has been reported to be in Roundup at levels of 0.2 - 0.4 ppm. NNG has been subjected to a hazard assessment review (see 8/24/78 memo of R. Taylor, FUS to DAA, OPP) with the result that OPP does not bar the establishment of glyphosate tolerances because of the presence of NNG (as per 9/5/78 R. Taylor memo).

[] is present as an impurity in a surfactant used in Roundup. TOX has withheld their support from this petition until questions raised about this impurity are resolved. Little, if any, residue would be expected on fruit from the proposed use. [] is cleared for solvent use under 40 CFR 180.1001(d).

INERT INGREDIENT INFORMATION
DELETED

Proposed Use

The proposed use for glyphosate in guava and papaya orchards is the same as that established for other tree crops.

For the control of a variety of weeds Roundup is to be applied at rates of up to 5 quart/A. The combined total of all treatments must not exceed 10.6 quart/A (8 lb a.i./A) per year. Livestock are not to forage or feed on treated areas for 8 weeks after application. The PHI is one day. The label advises that extreme care must be exercised to avoid contact of spray drift or mist with green foliage, green bark or bark of trees established less than two years, suckers, or fruit of desirable trees.

Nature of the Residue

Radiotracer plant metabolism studies (corn, soybeans, wheat, cotton, rice, barley, oats, sorghum, sugarbeets, sugarcane, potatoes, vegetable crops, grapes, coffee and citrus orchard fruits) have been submitted in conjunction with several glyphosate petitions and were discussed in our reviews.

In all cases the major degradative pathway of glyphosate has been shown to entail C-N bond cleavage to form glyoxylate and the major metabolite aminomethylphosphonic acid (CP 50435). Further metabolism involves significant incorporation of fragments of these compounds into natural plant products.

From the proposed use, there is no application to the growing fruit. Any residue occurring in fruit from this use would be expected to be contaminative in nature.

Tracer studies (submitted with previous petitions) in rats, rabbits and cows indicate that most of the radioactive dose is excreted (90% within 5-7 days), primarily in the feces. The major component of the residue is the parent compound with only trace amounts of aminomethylphosphonic acid being found.

We conclude that the metabolism of glyphosate in plants and animals is adequately understood.

Analytical Methods

The method used for residue analysis for both guava and papaya is very similar to that used for enforcement. Glyphosate and its major metabolite, aminomethylphosphonic acid are determined separately.

Briefly, a plant sample is extracted (in a blender) with water-chloroform. The aqueous phase, which contains both compounds, is cleaned up on an ion exchange column and then with charcoal. The two compounds are separated via column chromatography on AG 50W-X8. Precise directions for elution (with deionized water) are followed in

order to obtain cleanly separated fractions. Trifluoroacetic anhydride is used to convert both compounds to the N-trifluoroacetyl methyl ester derivatives which are then determined by GLC using a phosphorus specific flame photometric detector.

Quava fruit fortified with 0.05 ppm N-phosphonomethylglycine gave recoveries of 22-62% (average = 43%); fortified with 0.05 ppm aminomethylphosphonic acid the recovery was 50-72% (average = 61%).

Papaya fruit fortified with 0.05 ppm N-phosphonomethylglycine gave recoveries of 31-62% (average = 51%); fortified with 0.05 ppm aminomethylphosphonic acid the recovery was 47-90% (average = 71%). All check values (for either compound from either fruit) were <0.05 ppm.

The recovery values, especially those for glyphosate, would, under normal circumstances render an analytical method too tenuous to be of value for enforcement purposes. However since glyphosate is not to be applied to guava foliage or fruit (in addition to the label warnings the herbicidal potency of Roundup mitigates against this type of misuse) and therefore no residue is expected in the fruit, we will consider this validation data to be adequate.

The claimed sensitivity of 0.05 ppm for either compound is supported by accompanying chromatograms.

A successful HPLC method tryout for glyphosate on peanuts has recently been completed (PP#OF2329, memo of 1/19/81 R.W. Storherr). Earlier, a similar method has been successfully tried out on tomatoes and cottonseed (memo of 9/19/80, R.W. Storherr). The HPLC methods are less time consuming but not as sensitive as the method used to gather data for guavas and papayas and are suitable for confirmatory analysis.

We conclude that adequate analytical methods are available for enforcement purposes.

Residue data

Guavas

Experiments to determine residues of glyphosate in guavas were carried out at two locations in Hawaii, Waimanalo and Malamaki.

Three applications of either 2 or 8 lbs a.i./A were made to the floors of guava orchards. The highest proposed rate is 10.6 qts/A/year (8 lbs a.i./A/year) in applications of no more than 5 qts/A (3.8 lb/A) each. No residues (<0.05 ppm) of either the parent or aminomethylphosphonic acid were found at PHI's of either 1 or 14 days.

From the proposed use we expect no detectable glyphosate residues in guavas.

Papayas

Experiments to determine residues of glyphosate on papayas were also carried out at two Hawaiian locations, Pomoaho and Keaau.

Three applications of either 1, 2, 4 or 8 lbs a.i./A were made to the floors of papaya orchards. No residues (<0.05 ppm) of either the parent or aminomethylphosphonic acid were found at PHI's of 1 or 14 days.

We do not expect any detectable residues of glyphosate in guavas from the proposed use.

Meat, Milk, Poultry and Eggs

Since no feed items are involved, there will be no problem of secondary residues in meat, milk, poultry and eggs.

cc: Reading file

Circu

Reviewer

FDA

PP# No.

TOX

EEB

EFB

Randy Watts

TS-769:Reviewer:K.Arne:LDT:X77324:CM:#2:RM:810:Date:2/9/81
EDI:Section Head:RSQuick:2/12/81:RDS:Date:2/12/81

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INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Glyphosate

PETITION NO 1E2443

CCPR NO. - (Roundup)

Codex Status

Proposed U. S. Tolerances

☒ No Codex Proposal
Step 6 or above

Residue (if Step 9):

Residue: parent +

None

aminomethylphosphonic acid

Crop(s) Limit (mg/kg)

Crop(s) Tol. (ppm)

Guava 0.2 ppm

CANADIAN LIMIT

MEXICAN TOLERANCIA

Residue:

Residue: None

N-(phosphonomethyl) glycine

Crop Limit (ppm)

Crop Tolerancia (ppm)

stone fruit
citrus 0.1 ppm
grapes

None

Notes:

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Glyphosate

PETITION NO 1E2444

CCPR NO. - (Roundup)

Codex Status

☒ No Codex Proposal
Step 6 or above

Residue (if Step 9):

None

Crop(s) Limit (mg/kg)

Proposed U. S. Tolerances

Residue: parent +
aminomethylphosphonic acid

Crop(s) Tol. (ppm)

Guava 0.2 ppm

CANADIAN LIMIT

Residue:

N-(phosphonomethyl) glycine

Crop Limit (ppm)

stone fruit
citrus 0.1 ppm
grapes

MEXICAN TOLERANCIA

None

Residue:

Crop Tolerancia (ppm)

None

Notes:

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